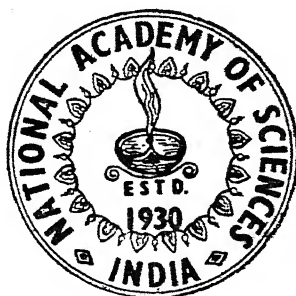


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Part II



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SECTION - A

PART II

DIFFUSION OF ANIONIC METAL TARTRATE COMPLEXES
THROUGH FILTER PAPER

PART I. AQUEOUS ETHANOL AS SOLVENT

By

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[Received on 11th May 1959]

ABSTRACT

In this paper we have reported our results on the attempted separation of copper (II), nickel (II), cadmium (II) and cobalt (II) in mixtures by filter paper strip chromatography, using aqueous ethanol as solvent. The effect of the presence of varying concentrations of tartrate ion as a complexing agent in the mixtures has been studied. The complexing agent has been added in the metal solution, and not in the solvent as usually done by previous workers. The R_F values and therefrom the R_M values have been calculated. In order to examine the possibility occurs, the R_L and R_T values have been calculated and reported in every case.

It has been observed that, in general, when two metals are present, the separations occurs upto 0.9 equivalents of added tartrate ions (ratio total metal : tartrate 1 : 0.9). When the tartrate is increased to 1.0 equivalents or further, no separation occurs. In the case of three metals present together, for good separation upto 0.6 equivalents of tartrate may be added. Excess of tartrate leads to overlapping of zones.

It is well known, that complex formation plays an important role in the separation of ions in chromatography Pollard and coworkers^{1,2} pointed out that for the separation of metallic ion on filter paper the formation of complexes is essential. The study of the separation of inorganic ions by paper chromatography with different solvent mixtures with or without the help of complexing agents is largely due to the work of Burstall³ *et al* and Lederer.⁴ In earlier papers⁵⁻⁸ we have described the studies on the diffusion of complex ions formed by the interaction of metallic ions with the carboxylic acid groups, *viz.*, oxalate, tartrate and citrate by filter paper chromatography. The solvent used in the studies was aqueous ethanol. We have also shown the variation of R_F values of the ions formed in

mixtures having different proportions of the metal ion and complexing agent, with a view to determining the effect of varying concentrations of the complexing agent in the diffusion process.

In this paper the work has been extended to mixtures also and attempts have been made to employ complex-formation with tartrate in the separation of ions by strip filter paper chromatography using aqueous ethanol as solvent. The mixture of the ions Cu^{++} , Ni^{++} , Co^{++} and Cd^{++} have been so investigated.

In order to understand whether a good separation is possible in mixtures and that whether overlapping is occurring between two ions, R_T and R_L values are often useful.⁹ The R_L and R_T values represent, respectively the ratio of the movement of the leading edge to the solvent front and that of the trailing edge to the solvent front. The R_F values in each case were determined experimentally as described earlier.⁵ Also the R_F value permits the calculation of R_M value by the relation $R_M = \log \left(\frac{1}{R_F} - 1 \right)$ proposed by Bate-Smith and Westall¹⁰ and we have recorded the $-R_M$ values in the tables instead of R_F values.

EXPERIMENTAL

Solutions of cupric sulphate, nickel sulphate, cobalt sulphate and cadmium chloride were prepared using BDH AnalaR grade chemicals and standardised as usual. A standard stock solution of sodium tartrate was prepared and diluted as necessary. All other reagents used were of reagent quality. Strips of Whatman filter paper No. 1 were used for the chromatograms. A simple ascending filter paper strip method as described by Gage Douglass and Wender¹¹ was used. Various concentrations of aqueous ethanol were tried and it was found that 50% ethanol was suitable as solvent in all the cases except in Table III where 60% ethanol was more efficient as it gave better separation. A series of mixtures was prepared by taking equal concentrations of the metals and adding varying quantities of tartrate solution while keeping the total volume constant. In column 2 the ratio total concentration of the metals (obtained by adding the concentration in molarity of the metals) to the concentration of tartrate is expressed. The mixtures were spotted on these strips. The chromatograms were run at constant temperature in a thermostatic controlled room at 30°C and time allowed was 90 minutes. A large number of experiments were conducted and some of the typical results are summarised here.

Separation of Cobalt (II) and Cadmium (II)

TABLE I

Final concentration of each of the metal ions = 0.05 M
(H_2S water used for developing)

No.	Ratio Total : Tart ²⁻ - metal	Values of Cobalt (II)			Values of Cadmium (II)		
		$-R_M$	R_L	R_T	$-R_M$	R_L	R_T
1	1 : 0	0.86	0.93	0.90	0.75	0.90	0.0
2	1 : 0.1	0.78	0.91	0.88	0.68	0.88	0.0
3	1 : 0.2	0.68	0.88	0.86	0.63	0.86	0.0
4	1 : 1.0	0.68	0.88	0.51		No movement	
5	1 : 1.3	0.68	0.88	0.57		No movement	
6	1 : 1.5	0.68	0.88	0.58		No movement	
7	1 : 2.0	0.68	0.88	0.58		No movement	
8	1 : 2.5	0.68	0.88	0.58		No movement	
9	1 : 3.0	0.68	0.88	0.58		No movement	
10	1 : 4.0	0.68	0.88	0.58		No movement	
11	1 : 5	0.68	0.88	0.58		No movement	

In the above table, we find that separation of cobalt (II) and cadmium (II) occurs at all the concentrations of tartrate recorded here. However, when the ratio of metal : concentration of tartrate is 1 : 0.3 to 1 : 0.9, there is no separation of the ions and so the results have not been shown. With a ratio of 1 : 1.0 and above there is no movement of cadmium (II) and only cobalt (II) diffuses upwards. It may be noted that in the case of cobalt (II) the R_M and R_L values decrease and become constant as 0.2 equivalents of tartrate are added. The R_T values, however, decrease at first but finally increase again to attain constancy. In the case of cadmium (II) there is always a tailing as seen from the R_T values = 0.0. For separation a concentration 1 : 1 of tartrate is recommended where the separation is satisfactory.

Separation of Cadmium (II) and Copper (II)

TABLE II

Final concentration of each of the metal ions = 0.05 M
(Freshly prepared a mixture of H_2S water and $K_4Fe(CN)_6$
used for developing.)

No.	Ratio Total : Tart ²⁻ - metal	Values of Cadmium (II)			Values of Copper (II)		
		$-R_M$	R_L	R_T	$-R_M$	R_L	R_T
1	1 : 0	0.75	0.86	0.83	0.55	0.83	0.00
2	1 : 0.1	0.75	0.86	0.77	0.41	0.77	0.00
3	1 : 0.2	0.72	0.86	0.74	0.35	0.74	0.40
4	1 : 0.3	0.63	0.86	0.72	0.25	0.69	0.44
5	1 : 0.4	0.45	0.84	0.70	0.25	0.68	0.47
6	1 : 0.5	0.45	0.83	0.67	0.23	0.67	0.52
7	1 : 0.6	0.43	0.81	0.67	0.21	0.67	0.54
8	1 : 0.7	0.43	0.81	0.67	0.21	0.67	0.54
9	1 : 0.8	0.33	0.70	0.66	0.19	0.66	0.55
10	1 : 0.9	0.33	0.70	0.65	0.17	0.65	0.55

In the above cases precipitation is found to occur. Redissolution of the precipitate is only complete when 1.7 equivalents of tartrate are added, but beyond, 0.9 equivalents no separation is possible. But, it may be seen that good separation of the ions from the supernatant liquid is obtained when 0.3 to 0.4 equivalents of tartrate are added, though a part remains settled as a precipitate. The R_L value in the case of cadmium (II) does not change up to 0.3 equivalents of tartrate and by further increasing the concentration of tartrate the R_L value tends to decrease and constantly decreases until it becomes 0.70 with 0.9 equivalents of tartrate. It is noted that the R_L value of Cu^{++} decreases with the addition of tartrate and then gradually decreases with high concentrations of the same. It has been noted that the R_T value of Cu^{++} increases as the concentration of tartrate increases and finally tend to become constant with high concentration of tartrate ions.

Separation of Cadmium (II) and Nickel (II)

TABLE III

Final concentration of each of the metal ion = 0.05 M
(A mixture of H₂S water and dimethyl glyoxime used for developing).

No.	Ratio Total : Tart ²⁻ - metal	Values of Cadmium (II)			Values of Nickel (II)		
		-R _M	R _L	R _T	-R _M	R _L	R _T
1	1 : 0.5	0.41	0.84	0.59	0.09	0.59	0.00
2	1 : 0.6	0.41	0.84	0.59	0.09	0.59	0.00
3	1 : 0.7	0.39	0.82	0.57	0.05	0.57	0.00
4	1 : 0.8	0.39	0.81	0.56	0.03	0.56	0.00
5	1 : 0.9	0.39	0.81	0.56	0.03	0.56	0.00

It was noted from observations not recorded here that there is no separation of the ions when 0.1 to 0.4 equivalents of tartrate are added. It may be seen that good separation of the ions is obtained when 0.7 to 0.8 equivalents of the complexing agent are used. No separation is possible beyond 0.9 equivalents of tartrate because of the spreading and overlapping of zones. It may be noted from the observations recorded in Table III that with the addition of tartrate the R_L and R_M values of Cd⁺⁺ and Ni⁺⁺ decrease constantly with increasing concentrations of the complexing agent and have a tendency to become constant with higher concentrations of tartrate. In case of nickel (II) the R_T value is zero.

Separation of Copper (II) and Nickel (II)

TABLE IV

Final concentration of each of the metal ions = 0.05 M
(A mixture of potassium ferrocyanide and dimethyl glyoxime used for developing).

No.	Ratio Total : Tart ²⁻ - metal	Values of Nickel (II)			Values of Copper (II)		
		-R _M	R _L	R _T	-R _M	R _L	R _T
1	1 : 0	0.78	0.88	0.84	0.60	0.84	0.00
2	1 : 0.1	0.72	0.87	0.80	0.55	0.80	0.00
3	1 : 0.2	0.65	0.86	0.78	0.45	0.78	0.00
4	1 : 0.3	0.63	0.86	0.78	0.43	0.76	0.00
5	1 : 0.4	0.60	0.85	0.75	0.39	0.74	0.20
6	1 : 0.5	0.60	0.83	0.73	0.37	0.73	0.42
7	1 : 0.6	0.60	0.83	0.73	0.37	0.73	0.44
8	1 : 0.7	0.50	0.79	0.73	0.37	0.73	0.44
9	1 : 0.8	0.50	0.79	0.73	0.37	0.73	0.44
10	1 : 0.9	0.45	0.75	0.73	0.37	0.73	0.44

In the beginning precipitation of the tartrates occurred in the systems and when about 0.9 equivalents of tartrate were added, total redissolution of the precipitate occurred. The separation of the ions is possible up to 0.9 equivalents of tartrate added, but with higher concentrations no separation occurs and so the results have not been shown. A good separation is effected when 0.3 to 0.4 equivalents of the complexing agent are used. It may be noted from the observations recorded in Table 4 that the R_L and R_M value of nickel (II) decreases by small additions of tartrate and continues to decrease with higher concentration of the complexing agent. The R_L and R_M values of Cu^{++} decrease with the addition of tartrate and finally become constant with 0.5 equivalents of tartrate. The R_T value of Cu^{++} is zero upto 0.3 equivalent of tartrate but by increasing the concentration of tartrate it increases and finally becomes constant.

Separation of Cobalt (II) and Copper (II)

TABLE V

Final concentration of each of the metal ions = 0.05 M

(A freshly prepared mixture of H_2S water and $K_4Fe(CN)_6$ used for developing).

No.	Ratio Total : Tart ²⁻ metal	Values of Cobalt (II)			Values of Copper (II)		
		$-R_M$	R_L	R_T	$-R_M$	R_L	R_T
1	1 : 0	0.68	0.86	0.80	0.48	0.80	0.00
2	1 : 0.1	0.60	0.84	0.75	0.37	0.75	0.00
3	1 : 0.2	0.60	0.84	0.75	0.35	0.74	0.00
4	1 : 0.3	0.60	0.84	0.70	0.23	0.68	0.14
5	1 : 0.4	0.60	0.84	0.70	0.23	0.68	0.20
6	1 : 0.5	0.60	0.84	0.71	0.25	0.71	0.40
7	1 : 0.6	0.60	0.84	0.74	0.35	0.74	0.41
8	1 : 0.7	0.57	0.83	0.74	0.35	0.74	0.41
9	1 : 0.8	0.55	0.82	0.74	0.35	0.74	0.41
10	1 : 0.9	0.55	0.82	0.74	0.35	0.74	0.40

In the above cases precipitation is found to occur and the total redissolution of the precipitate occurs when 2.2 equivalents of the complexing agent are used. From Table V it may be seen that the separation of copper (II) and cobalt (II) ions is possible upto 0.9 equivalents of the complexing agent added, and with the higher concentration of the same the separation is not possible under the experimental conditions. A good separation is effected with the addition of 0.3 to 0.4 equivalents of complexing agent. The R_L and R_M values of cobalt decrease with the addition of the complexing agent and by increasing the concentration of the same the values have a tendency to become constant. In case of copper (II) the R_L and R_M values decrease with the addition of tartrate and as the concentration increases the values very slightly increase and then become constant with high concentration of the same. R_T value of copper (II) attains constancy with high concentration of the complexing agent.

Separation of Nickel (II) and Cobalt (II)

In these ions no separation occurs because both the ions move simultaneously and have nearly the same R_F values. But both the ions can be detected together by spraying a mixture of dimethyl glyoxime and H_2S water and finally by exposing the chromatograms to vapours of ammonia.

Separation of Cobalt (II), Cadmium (II) and Copper (II)

TABLE VI

Final concentration of each of the metal ions = 0.055 M

(Indicator used a mixture of H_2S water and potassium ferrocyanide, freshly prepared).

No.	Total metal	Ratio : Tart ²⁻	Values of Cobalt (II)			Values of Cadmium (II)			Values of Copper (II)		
			$-R_M$	R_L	R_T	$-R_M$	R_L	R_T	$-R_M$	R_L	R_T
1	1	: 0	0.90	0.93	0.85	0.68	0.85	0.81	0.50	0.81	0.00
2	1	: 0.059	0.78	0.88	0.83	0.63	0.83	0.78	0.43	0.78	0.00
3	1	: 0.118	0.72	0.86	0.83	0.60	0.83	0.76	0.37	0.76	0.00
4	1	: 0.177	0.72	0.86	0.83	0.60	0.83	0.76	0.37	0.76	0.00
5	1	: 0.236	0.68	0.85	0.82	0.57	0.82	0.67	0.21	0.67	0.29
6	1	: 0.305	0.68	0.85	0.80	0.52	0.80	0.66	0.17	0.66	0.34
7	1	: 0.354	0.65	0.84	0.79	0.48	0.79	0.66	0.17	0.66	0.44
8	1	: 0.413	0.65	0.84	0.79	0.48	0.79	0.66	0.17	0.66	0.54
9	1	: 0.472	0.63	0.83	0.78	0.45	0.78	0.66	0.17	0.66	0.56
10	1	: 0.481	0.63	0.83	0.78	0.45	0.78	0.66	0.17	0.66	0.57

No precipitation occurs with 0.05 to 0.177 equivalents of tartrate added but with higher concentration of the complexing agent precipitation occurs in the system after the solution is allowed to stand. The separation of copper (II), cobalt (II) and cadmium (II) ions is possible upto 0.481 equivalents of tartrate added and with higher concentrations of the complexing agent the separation is not possible under the experimental conditions. From table VI, it is noted that the R_L and R_M values of Co^{++} , Cd^{++} and Cu^{++} decrease with the addition of tartrate and have a tendency to become constant with higher concentration of the same. The R_T value of Cu^{++} increases with the concentration of the complexing agent.

Separation of Copper (II), Cadmium (II) and Nickel (II)

TABLE VII

Final concentration of each of the metal ions = 0.055 M
(H₂S water, K₄F₆, (CN)₆ and dimethyl glyoxime used as indicator.)

No.	Ratio Total metal : Tart 2-	Values of Cadmium (II) and Nickel (II)			Values of Copper (II)		
		-R _M	R _L	R _T	-R _M	R _L	R _T
1	1 : 0	0.72	0.86	0.82	0.48	0.82	0.00
2	1 : 0.059	0.63	0.82	0.80	0.45	0.80	0.00
3	1 : 0.118	0.60	0.82	0.76	0.39	0.76	0.00
4	1 : 0.177	0.60	0.83	0.76	0.39	0.76	0.00
5	1 : 0.236	0.55	0.83	0.71	0.27	0.71	0.26
6	1 : 0.305	0.55	0.84	0.71	0.27	0.71	0.37
7	1 : 0.354	0.55	0.84	0.71	0.27	0.71	0.44
8	1 : 0.413	0.60	0.85	0.71	0.27	0.71	0.44
9	1 : 0.472	0.60	0.85	0.71	0.27	0.71	0.45
10	1 : 0.481	0.60	0.85	0.71	0.27	0.71	0.45
11	1 : 0.590	0.60	0.85	0.71	0.27	0.71	0.45

In the beginning no precipitation occurs in the system and when about 0.177 or more equivalents of the complexing agent are added the precipitation occurs after the solution is allowed to stand. In the separation of Cu⁺⁺, Cd⁺⁺, and Ni⁺⁺ ions only the separation of Cu⁺⁺ ion is possible upto 0.59 equivalent of the complexing agent, and with higher concentration the separation is not possible. In this case R_L, R_M and R_T values of Cu⁺⁺ behave in a similar manner as in Table VI.

Separation of Cobalt (II), Nickel (II) and Copper (II)

TABLE VIII

Final concentration of each of the metal ions = 0.055 M
(Potassium ferrocyanide and dimethyl glyoxime used as indicator)

No.	Ratio Total metal : Tart 2-	Values of Nickel (II) and Cobalt (II)			Values of Copper (II)		
		-R _M	R _L	R _T	-R _M	R _L	R _T
1	1 : 0	0.78	0.90	0.80	0.48	0.80	0.00
2	1 : 0.059	0.55	0.84	0.72	0.31	0.72	0.00
3	1 : 0.118	0.55	0.84	0.70	0.27	0.70	0.00
4	1 : 0.177	0.57	0.85	0.69	0.25	0.69	0.00
5	1 : 0.236	0.57	0.85	0.69	0.25	0.69	0.29
6	1 : 0.305	0.57	0.85	0.69	0.25	0.69	0.37
7	1 : 0.354	0.57	0.85	0.67	0.21	0.67	0.41
8	1 : 0.413	0.57	0.85	0.67	0.21	0.67	0.41
9	1 : 0.472	0.57	0.85	0.67	0.21	0.67	0.42
10	1 : 0.481	0.57	0.85	0.67	0.21	0.67	0.42
11	1 : 0.590	0.57	0.85	0.67	0.21	0.67	0.42

No precipitation occurs with 0.059 to 0.177 equivalents of the complexing agent but with higher concentrations of the same precipitation occurs after the solution is allowed to stand for a long time. In the separation of Ni^{++} , Co^{++} and Cu^{++} ions, only the separation of Cu^{++} is possible upto 0.59 equivalents of the complexing agent added, and with a higher concentration of the same no separation takes place. The R_L , R_M and R_T values of Cu^{++} behave in a similar manner as recorded before.

Separation of Nickel (II), Cobalt (II), Cadmium (II) and Copper (II)

TABLE IX

Final concentration of each of the metal ions = 0.042 M

(Potassium ferrocyanide, H_2S water and dimethyl glyoxime used for developing.)

No.	Ratio Total metal : Tart 2-	Values of Cobalt (II), Nickel (II), Cadmium (II)			Values of Copper (II)		
		$-R_M$	R_L	R_T	$-R_M$	R_L	R_T
1	1 : 0	0.75	0.90	0.81	0.48	0.81	0.00
2	1 : 0.05	0.75	0.90	0.79	0.45	0.79	0.00
3	1 : 0.10	0.72	0.90	0.76	0.39	0.76	0.00
4	1 : 0.15	0.72	0.90	0.74	0.35	0.74	0.12
5	1 : 0.20	0.72	0.90	0.71	0.27	0.71	0.42
6	1 : 0.25	0.72	0.90	0.71	0.27	0.71	0.42
7	1 : 0.30	0.65	0.88	0.71	0.27	0.71	0.43
8	1 : 0.35	0.65	0.88	0.71	0.27	0.71	0.44
9	1 : 0.40	0.65	0.88	0.71	0.27	0.71	0.47
10	1 : 0.45	0.65	0.88	0.71	0.27	0.71	0.48
11	1 : 0.50	0.63	0.87	0.71	0.27	0.71	0.51
12	1 : 0.65	0.60	0.85	0.71	0.27	0.71	0.51

No precipitation occurs with 0.05 to 0.15 equivalents of the tartrate added and in the rest precipitation is observed. The separation of copper (II) ions only from Co^{++} , Ni^{++} and Cd^{++} ion is possible upto 0.65 equivalents of tartrate added. No separation is possible with higher concentration of tartrate.

Separation of Nickel (II), Cobalt (II) and Cadmium (II)

No satisfactory separation of nickel (II), cobalt (II) and cadmium (II) ions is possible with ethanol as solvent due to the spreading and the overlapping of zones.

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POLAROGRAPHY OF THIOMALIC ACID (PART I)

By

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ABSTRACT

The polarography of thiomalic acid in the reduced form has been studied. Well defined anodic waves have been obtained in pH range 1—9. Normal diffusion currents have been observed over this entire pH range. Analysis of the anodic wave in borax buffer (pH 9.2) indicates one electron change during the electrode reaction. At 0.005 M and higher concentrations anodic maxima have been observed which are suppressed by the addition of gelatin.

A number of organic sulphydryl and disulphide compounds like cystein, cystine^{1,2,3,4}, glutathione⁵ and thioglycolic acid⁶ have been studied polarographically. These compounds have also been employed to reduce the disulphide groups in proteins.⁷ A large degree of interest has been shown recently in these and other related compounds.

Thiomalic acid is a sulphydryl compound similar to the above mentioned group. Recently some interest has been shown in the usefulness of this compound. The authors have made a polarographic study of thiomalic acid. In this paper a preliminary study of its polarography has been described. Further work is in progress and shall be communicated at an early date.

MATERIALS

Thiomalic acid was obtained as a gift from Evans Chemetics Inc., New York (U. S. A.). The compound was 97% pure as determined amperometrically. Stock solutions of 0.1M and 0.01M thiomalic acid was prepared in double distilled water. Only freshly prepared solutions were used for investigations. All other chemicals used were of Analar or Chemically Pure grade. Mercury used in the Dropping Mercury Electrode (DME) was first purified by chemical treatment and subsequently distilled twice.

APPARATUS

Leeds & Northrup Electrochemograph was used in all the polarographic investigations. A manual set up was also used. The circuit was similar to the one described by Lingane and Kolthoff.⁸

EXPERIMENTAL

Current-voltage curves were usually made at $30.0^{\circ} \pm 0.1^{\circ}\text{C}$. Some measurements were also made at room temperature. All potentials were measured against the Saturated Calomel Electrode (SCE). A Hume and Harris Saturated Calomel Electrode⁹ was used as reference electrode in all experiments.

The characteristics of the DME capillary used were

$$m = 1.376 \text{ mg. sec.}^{-1}; t = 54.75 \text{ sec. (open circuit)};$$

$$m^{2/3} t^{1/6} = 2.411 \text{ mg.}^{2/3} \text{ sec.}^{-1/6}; h = 40 \text{ cms.}$$

The pH of the solutions was measured with a Leeds & Northrup pH meter using a general purposes glass electrode.

RESULTS AND DISCUSSIONS

Polarograms of thiomalic acid at different concentrations were obtained in buffers of pH ranging between 1 and 9. Throughout this pH region thiomalic acid gives well defined anodic wave in the concentration region of 10^{-3} M to $5 \times 10^{-5} \text{ M}$. At higher concentrations (0.005 M and above) anodic maximum has been observed. The anodic maximum of thiomalic acid can be clearly seen in Fig. 1.

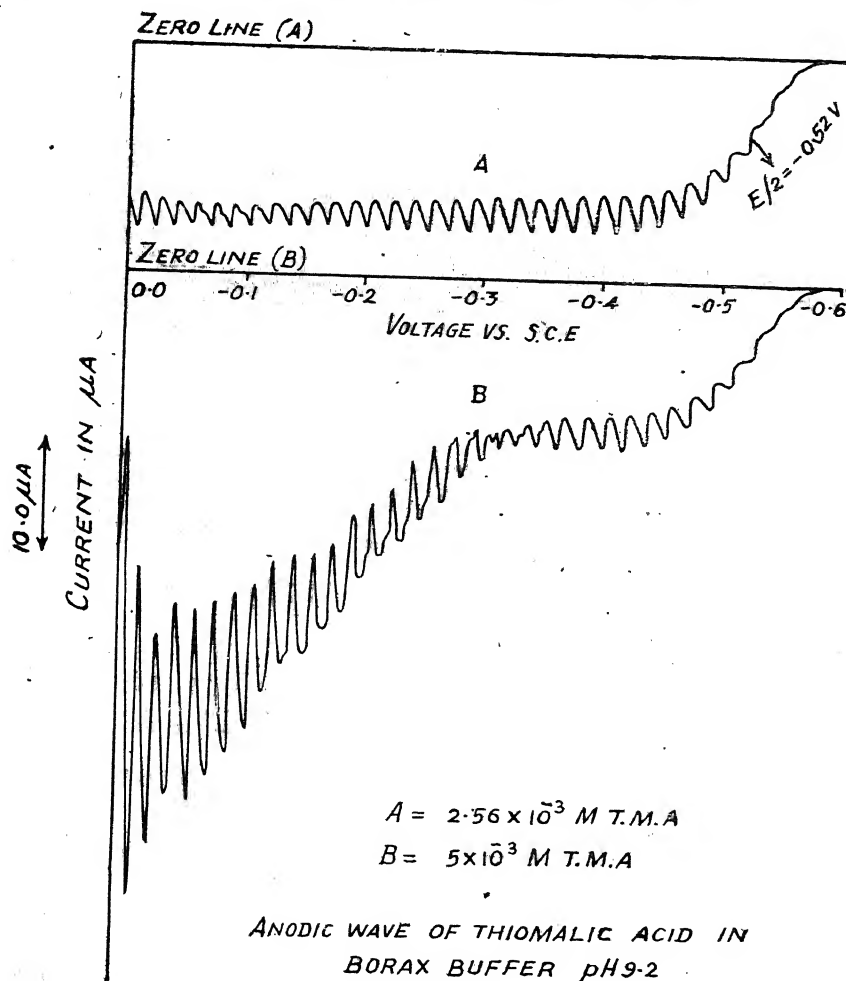


Fig. 1. Anodic wave of thiomalic acid in 0.05M borax, 0.1 M KCl ; pH 9.2.

Fig. 1.

The maximum can be suppressed by adding appropriate amount of gelatin. The progressive suppression of the maximum is shown in Fig. 2.

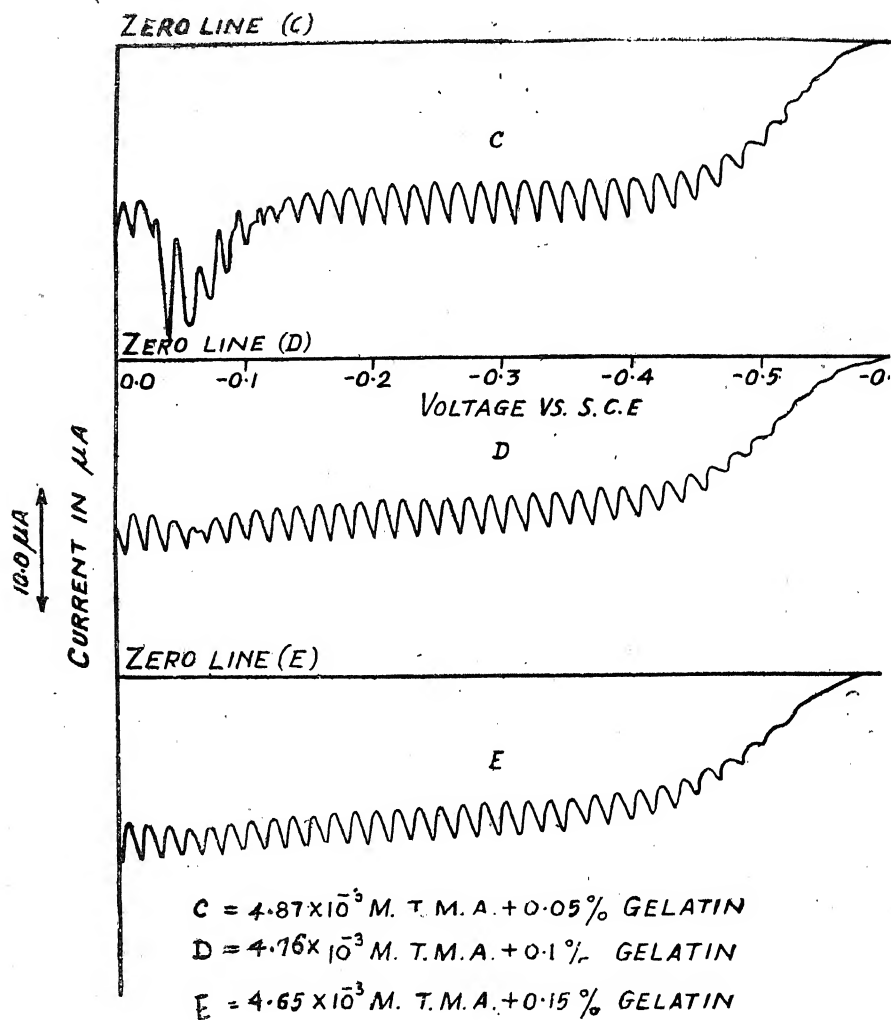


Fig. 2. Suppressing effect of gelatin on the anodic maximum of thiomalic acid in 0.05 M borax, 0.1 M KCl; pH 9.2.

Fig. 2.

A similar maximum effect has also been observed in ammonia buffer although in a less pronounced form (Fig. 3).

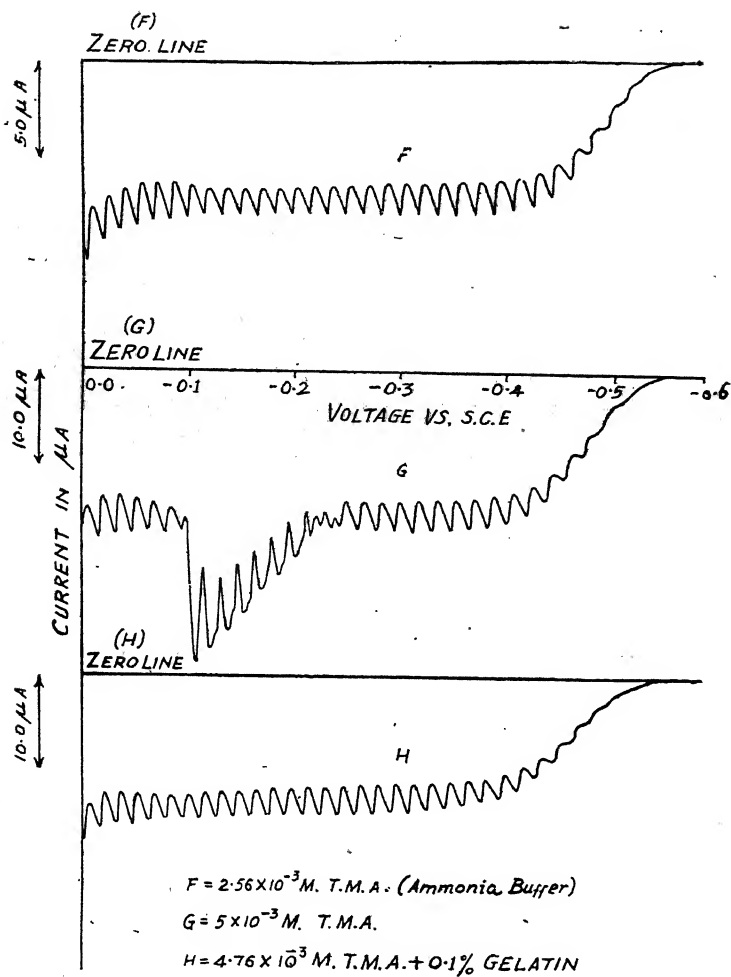


Fig. 3. Anodic wave of thiomalic acid in ammonia buffer ; pH 8.4.

Fig. 3.

Typical anodic waves in phosphate buffer (pH 7), acetate buffer (pH 5) and perchloric acid (pH 1) are shown in Fig. 4.

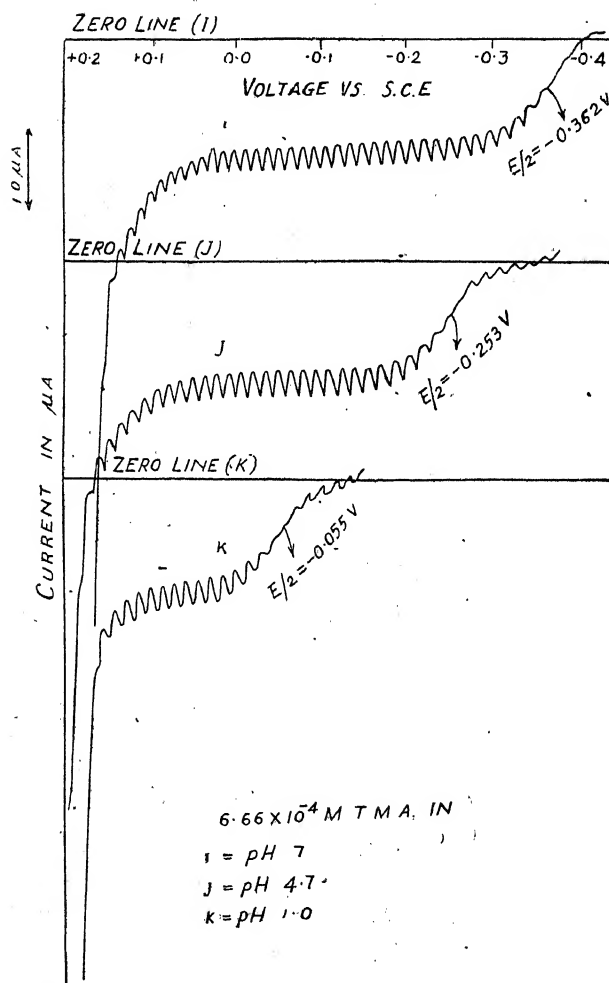


Fig. 4. Anodic wave of thiomalic acid; (I) Phosphate buffer; pH 7.0; (J) Acetate buffer; pH 4.7; (K) Perchloric acid; pH 1.3.

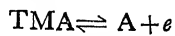
Fig 4.

A few representative c-v curves of thiomalic acid have been evaluated in the following table.

TABLE I

Buffer	pH	Concentration $M \times 10^3$ (C)	Current i_d in μA	i_d / C	$E_{1/2}$ in Volts.	Remarks
Borax + KCl	9.2	0.206	0.638 at $-0.25V$.	3.09	-0.505	at $30^\circ C$.
"	9.2	0.50	1.479 " "	2.96	-0.505	"
"	9.2	0.95	2.879 " "	3.03	-0.51	"
"	9.2	2.56	7.41 " "	2.9	-0.52	"
"	9.2	5.00	—	—	—	" Appearance of maximum.
$NH_4Cl + NH_4OH$	8.4	0.476	1.395 " "	2.93	-0.457	at $30^\circ C$
"	8.4	0.909	2.725 " "	2.99	-0.46	"
"	8.4	1.304	3.825 " "	2.93	-0.46	"
$NaH_2PO_4 + Na_2HPO_4$ }	7.2	0.666	1.50 at $-0.15V$.	2.25	-0.362	at Room Temp.
$CH_3COOH + CH_3COONa$ }	4.7	0.666	1.575 at $-0.05V$.	2.36	-0.253	" "
$HClO_4$	1.3	0.666	2.00 at $+0.05V$.	3.00	-0.055	" "

Analysis of the anodic wave of a solution of thiomalic acid in borax buffer (pH 9.2) was done. The plot of $\log (i_d - i)/i$ versus the potential gave a straight line with a slope of 0.061 V. This is very near to the theoretical value of 0.059 indicating one electron change reaction at the electrode. It is assumed that the reaction takes place in the following manner.



The equation of the anodic wave is thus given by the expression—

$$E = E_{1/2} - 0.059 \log (i_d - i)/i$$

ACKNOWLEDGEMENT

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ADSORPTION OF CRYSTAL VIOLET ON HYDROUS CHROMIUM OXIDE

PART I. NATURE OF ADSORPTION ISOTHERM

By

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ABSTRACT

It is well known that acid dyes containing a coloured anion, viz. alizarin is taken up by hydrous oxides of aluminium, chromium, iron etc. whilst a basic dye as methylene blue is taken up by acidic hydrous oxide as silica.

It is noted that basic dye crystal violet solution is a good adsorbate for hydrous chromium oxide prepared under suitable conditions. Ghosh and coworkers in their previous papers have observed hydrous oxide of chromium precipitated in the excess of caustic soda solution is capable of adsorbing cations and develop acidic properties.

The adsorption isotherms obtained have inflections, increases with increasing temperature and time. The adsorption curves indicate that :

1. The adsorption isotherm in initial stages is convex towards x axis, showing that the heat of adsorption is smaller than the heat of dissolution of crystal violet,
2. When saturation is reached, the adsorption is of unimolecular layer.
3. The adsorption of dye-stuff in solution is very similar to the gaseous adsorption.

The adsorption from aqueous solution of electrolytes by the hydrous oxides of iron, chromium, tin, aluminium etc. has been largely investigated¹. These hydrous oxides are also well known to form lakes² with dyestuffs. The nature of the hydrous oxides determine the taking up of acidic or basic dye. Hydrous chromium oxide is usually known as basic mordant, readily taking up acid dyes viz., orange II and alizarin. Blitz³ suggested that such lakes are not definite chemical compounds and Weiser⁴ opined that most lakes are adsorption complexes, the composition of which varies with the condition of formation.

According to Ghosh and coworkers,⁵ the hydrous oxide of chromium being amphoteric, its basic or acidic character can suitably be evoked by controlling the mode of its preparation, specially by regulating the amount of alkali added for the precipitation of hydrous oxide from chromium salt solutions. In the present series of papers we have dealt with different samples of hydrous oxide of chromium (A, B and C) and studied their adsorptive capacities for the basic dye-stuff crystal violet and the acid like congo red. Three samples A, B and C were prepared by adding calculated amounts of 10 per cent excess; equivalent and 10 per cent deficient amounts of alkali.

In the present paper, our observations on the taking up of crystal violet by different samples of hydrous oxides of chromium at 30°C are reported. The results show that :

1. The adsorption of crystal violet by the hydrous oxide is a slow process and takes 72 hours or more for complete saturation.

2. The adsorption isotherms drawn from the observations recorded at different intervals of time are convex to the concentration axis in the earlier stages i. e., they assume a S shaped curve. This nature of the curve has a tendency to become linear when saturation is reached.

3. It has been concluded that the adsorption of the dyestuffs is very similar to the gaseous adsorption on solid surfaces.

4. When saturation is reached, the adsorption is of unimolecular layer.

5. The hydrous oxide of chromium obtained by precipitating it with excess of alkali possesses a high adsorptive capacity for crystal violet showing that the hydrous oxide has developed acidic properties.

EXPERIMENTAL

E. Merck sample of crystal violet after being purified by successive recrystallisation with water and alcohol was used as an adsorbate for the adsorption experiments. The stock solution contained one gram of crystal violet per litre. The comparative measurements of dye concentrations were carried out by using a Klett-Summerson glass cell photoelectric colorimeter using green filter No. 54 (transmission 520-580 millimicrons). This instrument was first calibrated to read directly the transmission of the solution as compared with the blank.

Eight solutions of different concentrations were prepared by diluting 5 ml to 40 ml of 0.01% crystal violet solution to 100 ml. in eight 100 ml. flasks. The estimations were carried out by diluting further 5 ml. of the above solutions to 30 ml. It was found that Beer's law holds good for these dilutions. At higher concentrations of the dye, Beer's law is not valid, possibly due to appearance of larger micelles with the increasing concentrations of the dye.

The effect of electrolyte *viz.*, barium chloride, strontium chloride, potassium sulphate and potassium chloride on the transmission through crystal violet was also studied. 10 ml. of 0.2 M electrolytes were mixed with 5 to 40 ml. of 0.01% crystal violet solution made upto 100 ml. in different 100 ml. flasks. It was noted that Beer's law also holds good in the presence of these electrolytes.

In strong alkaline solutions the colour of crystal violet solution fades quickly. However, in small alkalinity as in 0.1M sodium acetate, slight fading of the dye takes place when kept for a very long time. The faded colour of the dye can be restored by the addition of 5 ml. of acetic acid and sodium acetate buffer (pH 5.0 approx) to 5 ml. of the dye solution. In acidic medium the violet colour changes to blue but by the addition of 0.1M sodium acetate to 5 ml of blue crystal violet solution, the colour can be completely restored.

Thus through out the adsorption study, the estimation of the intensity of residual dye colour had been carried out in the presence of sodium acetate and acetic acid buffer so as to neutralise the effect of hydrogen ion concentration on the colour of the dye. All estimations were carried out by diluting the mixture of 5 ml of dye. 5 ml of buffer solution to 30 ml so as to bring the dye concentrations to a range where Beer's law is strictly valid.

A concentrated stock solution of chromium chloride was prepared and chromium and chloride contents were estimated by standard volumetric and gravimetric methods. Three samples A, B and C of the hydrous oxide were obtained at room temperature by precipitating fixed volume of chromium chloride solution with calculated amounts of standard sodium hydroxide solution in 10% excess, equivalent and 10% deficient amounts respectively. These samples were washed by decantation process with distilled water till the supernatant liquid gave no test for chloride ions. However, in sample C, the last traces of chloride ions could not be removed

completely due to increasing tendency of the hydrous oxide to peptise on continued washing. These precipitates were suspended in distilled water and stored in jena glass bottles.

It was noted that hydrous oxide peptises in the presence of dye and very fine suspension of hydrous oxide remained unsettled even on prolonged centrifuging. Hence the fine suspension was coagulated by the addition of 10 ml of 0.2M potassium sulphate to 20 ml of suspension. Thus for the adsorption study 20 ml of suspension and 10 ml of 0.2 M K_2SO_4 were taken in several 100 ml flasks. The whole solutions were diluted with 30 ml. distilled water. Measured volumes of 5 to 40 ml of 0.01% crystal violet solution were added and final volumes were quickly raised to 100 ml. The flasks were shaken well and kept at a constant temperature in a thermostat for attaining equilibrium. The supernatant liquids were taken out at different time intervals, centrifuged for 10 minutes and were estimated colorimetrically as discussed earlier in the presence of buffer. The results are plotted between end concentration and amount of dye adsorbed and the curves are given in figures Nos. 1 to 4.

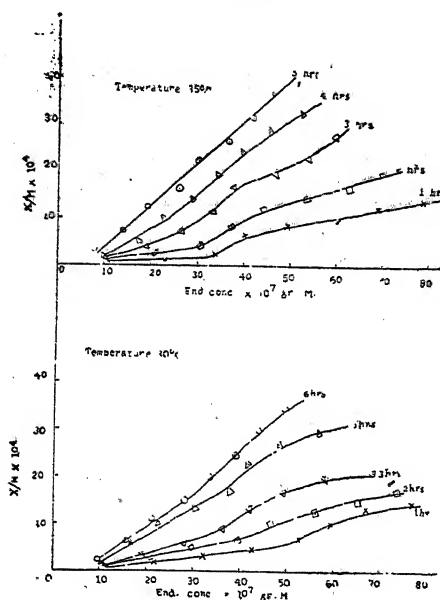


Fig. 1. Adsorption isotherm for crystal violet adsorption on hydrous chromium oxide sample A at 30°C & 35°C

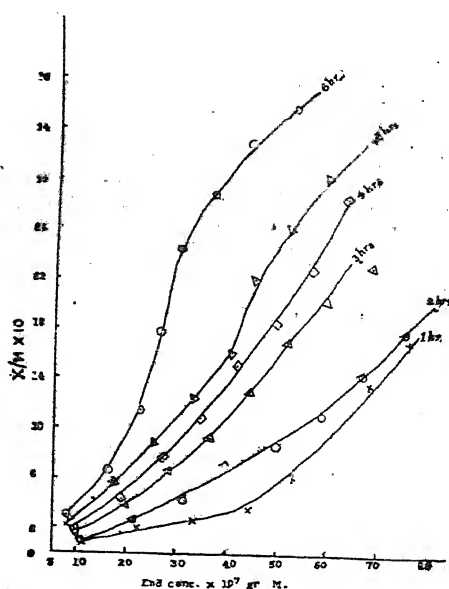


Fig. 2. Adsorption isotherm for crystal violet adsorption by hydrous chromium oxide sample B at 30°C

DISCUSSION

The adsorption isotherms as shown in the graphs for the adsorption of crystal violet by three different samples of hydrous chromic oxide are obtained by the estimation of dye upto six hours of contact. A fairly large amount of adsorption occurs within the first six hours but as much as 96 to 120 hours are required for complete saturation (Fig. 4).

The adsorption curves indicate deviation from ordinary adsorption isotherms specially when observations are taken for smaller duration of time. The curves are S shaped being convex to the concentration axis and very similar to the experimental data of Coolidge⁶ for the adsorption of water vapour by charcoal. This convex nature of the curve specially at lower concentrations of the dye, however,

vanishes with the increase in time of contact and temperature, as will be reported later. Langmuir's and Freundlich's equation of adsorption are not applicable for the range of concentrations investigated.

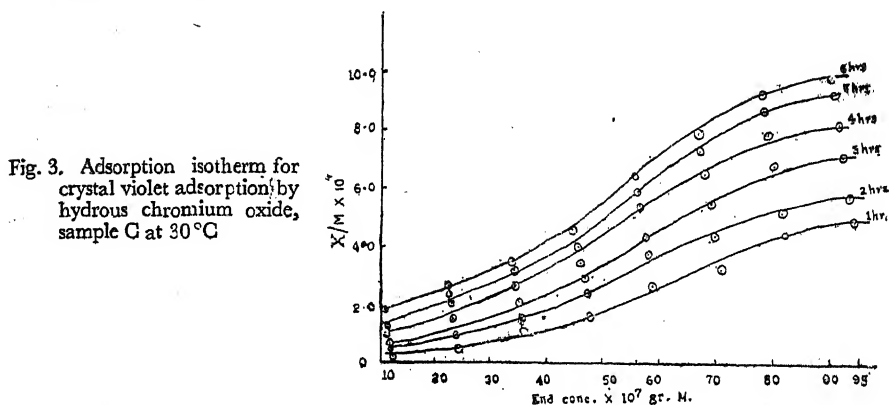


Fig. 3. Adsorption isotherm for crystal violet adsorption by hydrous chromium oxide, sample C at 30°C

An interesting fact is observed in the adsorption isotherms that at higher concentrations there is a tendency of a break in the adsorption isotherm. Such breaks are usual in multilayer adsorption of gases on solid surfaces but have rarely been observed in the case of solutions. Gyani⁷ has, however, reported similar breaks in the adsorption isotherms of some organic dyes by silica gel. It appears that the adsorption of dye from its solution by solids closely resembles the adsorption of gas on solids. It should be noted that at higher concentrations of the dye as that of crystal violet, the dye micelle is in an aggregated state, which decreases in solution. At higher concentrations of the dye the adsorption of aggregated micelle may occur, which is very similar to the formation of multi-molecular layer⁸ on the surface. It must be noted here that if prolonged time is allowed for attaining complete saturation for adsorption, the isotherm becomes completely linear, showing that the adsorption is of unimolecular layer type.

The observations recorded here lead to the conclusion that in the adsorption of crystal violet by hydrous chromium oxide, this occurs on the immediate contact of the dye solution with the solid surface. The chemisorption also becomes predominant at higher concentrations of the dye. This is supported by the fact that the adsorption isotherm has a tendency to be of the type of unimolecular layer with longer time of contact when saturation for adsorption is reached.

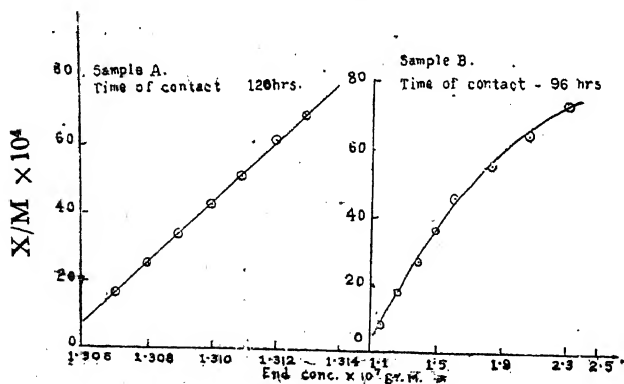


Fig. 4. Adsorption isotherm for crystal violet adsorption by hydrous chromium oxide sample A and B.

The convex shape of the isotherm at lower concentration of the dye towards the concentration axis, as has been noted here, is suggested to occur for the adsorption of a gas when its heat of liquefaction exceeds the heat of adsorption. According to B. E. T. concept of multimolecular layer⁸ the amount of gas adsorbed by the solid surface is given by the expression :

$$V = \frac{V_m \cdot c \cdot f}{1-f} \cdot \frac{1}{1+(c-1)f}$$

where V is volume of gas adsorbed at a given pressure P and at constant temperature, f is equal to $\frac{P}{P_0}$ where P_0 is vapour pressure at the experimental temperature, V_m is the vol of gas adsorbed to completely cover the surface of the first layer and C is approx. equal to $e^{E_1 - EL/RT}$ where E_1 is heat of adsorption of gas in the first layer and EL is heat of liquefaction of the gas. If $E_1 > EL$ a curve concave to the pressure axis is obtained. If E_1 is less than EL then the nature of the curve in the initial stage is convex to the pressure axis. The conclusion will be discussed in a subsequent paper.

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CHEMICAL EXAMINATION OF *TRICHOLEPIS PROCUMBENS*— A STUDY OF COLOURING MATTERS

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ABSTRACT

In the present investigation a colouring matter has been isolated from the plant *Tricholepis procumbens*. The colouring matter, provisionally named 'Procumbenin A' has the molecular formula $C_{34}H_{48}O_{11}$.

Tricholepis procumbens also known as *Volutarella divaricata*¹ N. O. Compositae (Hindi Badavard) is tonic and laxative cures old fevers and drives snakes away (Yunani). It is widely distributed throughout Central Western and Southern India, Baluchistan, Punjab plains and Afghanistan.

Tricholepis procumbens has been subjected to a systematic chemical examination. The plant was tested for both organic and inorganic substances. On complete incineration, the powdered plant gave greyish white ash which on analysis was found to contain sodium, potassium, aluminium, iron, calcium and magnesium as basic radicals and chloride, sulphate, carbonate and silicate as acid radicals.

Preliminary chemical examination of the plant showed the presence of a mixture of colouring matters and a mixture of reducing sugars. The alkaloids, saponins, oil, mucilage and free reducing sugars were found to be absent.

The colouring matters could be obtained by extracting the plant exhaustively with rectified spirit. From the crude residue obtained by distilling off the rectified spirit a colouring matter separated out in pure form could only be studied. Efforts are being made to collect the other three colouring matters in large quantities in a pure form.

The colouring matter provisionally named Procumbenin A is soluble in acetone ether, ethanol and methanol but is insoluble in petroleum ether, chloroform and benzene. It dissolves in caustic alkalis with a deep pink colour which changes to yellow colour on adding dilute hydrochloric acid and precipitates out on warming with more hydrochloric acid. It gives a bluish violet colour with ferric chloride in alcohol. It reduces Fehling's solution as such. When boiled with dilute hydrochloric acid for sometime the insoluble product does not reduce, while the filtrate reduces Fehling's solution indicating that the colouring matter is glucosidic in nature and reducing group is present in sugar molecule and not in aglycone. It decolorises alkaline potassium permanganate solution and bromine water.

The preliminary analysis shows that the colouring matter has the molecular formula $C_{34}H_{48}O_{11}$. It is found to contain two methoxy groups. On hydrolysis with dilute hydrochloric acid, glucose and a compound having molecular formula $C_{28}H_{32}O_6$ have been obtained. The aglycone procumbenidine ($C_{28}H_{32}O_6$) is found to contain two methoxy and three hydroxy groups.

The reducing sugars in the plant were found to be glucose, fructose, sucrose, lactose and maltose. The mixture of sugars were identified from the plant, on paper partition chromatographic examination.

EXPERIMENTAL

Extraction of the colouring matters :

3 Kgms. of the dry powdered plant was exhaustively extracted with rectified spirit. It was filtered hot and the hot alcoholic filtrate was allowed to cool. No solid substance was found to deposit. From the alcoholic extract, alcohol was distilled off under reduced pressure. The crude residue was boiled with water and filtered. This was done to remove water soluble impurities, tannins and reducing sugars (Portion B).

Portion A :

The crude product (Portion A) was then treated with 2.5% caustic soda and filtered. To the pink filtrate dilute hydrochloric acid was added and the mixture was warmed when a precipitate was obtained. This was filtrated and the product was then refluxed with acetone and filtered when two portions acetone soluble and acetone insoluble portions were obtained.

Acetone Soluble Part :

From acetone soluble part, acetone was distilled off and the residue was dissolved in ether. To the ether soluble part petroleum ether was added when a precipitate was obtained. This was filtered out and washed well with petroleum ether. It was again crystallised from acetone. This was provisionally named as Procumbenin A.

Acetone Insoluble Part :

Acetone insoluble part was washed well with acetone and then treated with benzene when two fractions benzene soluble (Procumbenin B) and benzene insoluble parts were obtained. Benzene insoluble part was then taken with ether when again two fractions were obtained, ether soluble (Procumbenin C) and ether insoluble part. From the ether insoluble part another product Procumbenin D was obtained by treating with absolute alcohol in which it was found soluble.

Procumbenin A :

Ultimate analysis of procumbenin A : Found : C, 65.2% and H, 6.9% ; molecular weight 634. $C_{34}H_{42}O_{11}$ requires C, 65.1% and H, 6.7% ; molecular weight, 626.

Methoxy Group :

Found : OCH_3 group (after Zeisal), 9.6%, $C_{34}H_{42}O_{11}$ requires for two methoxy groups, 9.9%

Properties of Procumbenin A :

Procumbenin A was found soluble in ethanol, methanol acetone, ethyl acetate and ether but insoluble in benzene, chloroform and petroleum ether.

It gave a bluish violet colour with ferric chloride in alcohol. It reduced Fehling's solution. If the compound was boiled with dilute hydrochloric acid for sometime and the solution filtered the insoluble product so obtained was found not to reduce the Fehling's solution while the filtrate after being neutralised with dilute caustic soda reduced the Fehling's solution.

The colouring matter dissolved in caustic alkalies with a pink colour which turned yellow on adding dilute hydrochloric acid. On warming for sometime a precipitate was obtained. It dissolved in concentrated sulphuric acid with a deep red colour.

With sodium bicarbonate it gave no effervescence thus indicating the absence of free carboxyl groups in the molecule.

Hydrolysis of Procumbenin A :

1.5 gms. of the compound Procumbenin A was refluxed with 30 c. c. of 25% hydrochloric acid for three hours. It was then filtered and the filtrate (Part B) was kept for sugar analysis. The insoluble residue aglycone (Part A) was washed well with hot water and was then dissolved in alcohol. The aglycone Procumbenidine was crystallised from benzene.

Found : C=72.8%, H=7.1%, molecular weight=473 calculated values for $C_{28}H_{32}O_6$, C=72.4%, H=6.8 molecular weight=464

Methoxy Groups : Found : OCH_3 group=13.7% calculated value for two methoxy groups=13.3%.

Tri-acetyl procumbenidine A :

0.5 gm. of the aglycone Procumbenine A was refluxed with sodium acetate (1.0 gm) and acetic anhydride (2.0 c. c.) for 5-6 hrs. The mixture was then poured in water when an oily liquid was obtained. It was kept overnight as such, when a solid substance was obtained. This solid substance was crystallised from ether. Molecular weight and acetyl groups were determined,

Found : acetyl groups=21.8% molecular weight=598.

Calculated values for $C_{40}H_{48}O_{14}$ - for three acetyl group=21.3%, molecular weight=590.

Part B :—The filtrate obtained as part B during the hydrolysis of the colouring matter was neutralised with dilute caustic soda and was concentrated under reduced pressure when a syrupy mass was obtained. This was shaken with methanol and filtered. Methanol soluble part was concentrated and the residue was taken in water. Chromatographic examination of the solution revealed the presence of glucose.

Portion 'B':—While extracting the colouring matters from the alcoholic extract of the plant, the water soluble portion so obtained was concentrated under reduced pressure. The concentrated solution was warmed with saturated solution of lead acetate when a yellow insoluble mass was obtained. It was filtrated and sulphuretted hydrogen was passed in the filtrate to remove excess of lead acetate. It was then filtered and the filtrate was concentrated under reduced pressure at 40°C to a syrup. The syrup was taken in distilled water (15 c.c.)

Chromatographic examination² of the solution showed the presence of glucose, fructose, sucrose, lactose and maltose. A number of chromatograms were developed and strips containing individual sugar were separately cut. Each set of strips of individual sugar was laxivated with hot water. Osazone derivatives were then prepared for each sugar. This confirmed the presence of the sugars.

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EFFECT OF POTASSIUM ION ON LOSS OF NITROGEN FROM AMMONIUM SULPHATE WHEN APPLIED TO SOIL ALONG WITH ORGANIC MATTER

By

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Crowther and Yates (1) have observed in their field experiments that when potassium and ammonium salts are added together to the soil as fertilizer, the yield was more than the sum of the increase in yield when the two were added individually. Russel (2) also observed increased yield when phosphorus and potassium salts were added along with ammonium salts than when ammonium salts were added alone. This may mean that when potassium salts were present along with ammonium salts, more nitrogen was available to the plants due to the saving of some nitrogen from being lost. The author has studied the effect of potassium ions in the form of potassium chloride on nitrogen loss from ammonium sulphate when added along with organic matter to the soil.

EXPERIMENTAL

The soil used for this experiment was collected from the field in front of Sheila Dhar Institute of Soil Science, University of Allahabad. The soil under study was light grey to brownish black in colour and alluvial in origin. Normal crops are grown on this. Its chemical composition was determined by the methods described by Piper (3) and A. O. A. C. (4). Top nine inches of the soil was collected and passed through a 100 mesh sieve after drying in air. An amount of oven dried soil was taken, to which, when organic matter in the form of cow-dung and/or potassium chloride were added, the total weight of the reacting moisture was 200 gms. The cow-dung was added as 0.5 % carbon. The reacting mixture was taken in 24 cm. diameter enamel dishes. Nitrogen was added at the rate of 43 lbs, 86 lbs and 129 lbs per acre as ammonium sulphate. 1 % of potassium chloride was added to see the effect of potassium ions on nitrogen loss from ammonium sulphate. The mixture was stirred on alternate days to make it homogenous and the moisture content was maintained at 20-25 % by adding distilled water. This was kept in the Laboratory at 27°C and samples were analysed after definite intervals for total carbon (5) and total nitrogen (6, 7).

The results obtained are recorded below :—

TABLE 1

Percentage composition of the soil used :

Silica (HCl insoluble)	...	78.4010
Loss on ignition	...	2.1030
Sesquioxides	...	11.3750
Ferric oxide	...	4.5200
Calcium oxide	...	3.3180
Magnesium oxide	...	1.6403
Potassium oxide	...	1.4700
Total phosphate	...	0.2193
Available phosphate (1 % citric acid)	...	0.0385
Aluminium oxide	...	6.8550
Exchangeable calcium	...	6.66 m. e. %
Total carbon	...	0.1527
Total nitrogen	...	0.0347
C/N ratio	...	4.4
Ammoniacal nitrogen	...	0.0026
Nitrate nitrogen	...	0.0017
Total available nitrogen	...	0.0043
Total/available nitrogen	...	8.0
pH	...	7.2

TABLE 2

Percentage composition of cow-dung used :—

Loss on ignition	...	63.46
Ash	...	36.53
Silica	...	30.66
Calcium oxide	...	2.52
Magnesium oxide	...	0.93
Potassium oxide	...	0.72
Total phosphate	...	0.67
Total carbon	...	28.63
Total nitrogen	...	1.0108
C/N ratio	...	28.34

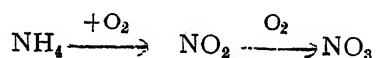
TABLE 3

Effect of potassium ion on loss of nitrogen from ammonium sulphate when added to soil:—

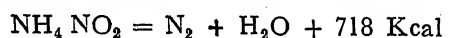
Treatment	% loss of nitrogen at the end of 60 days	% loss of nitrogen at the end of 120 days
Soil + cow dung + 43 lbs N per acre	20.1	39.9
Soil + cow dung + 43 lbs N per acre + 1 % KCL	19.5	39.4
Soil + cow dung + 86 lbs N per acre	22.2	41.2
Soil + cow dung + 86 lbs N per acre + 1 % KCL	21.8	40.6
Soil + cow dung + 129 lbs N per acre	24.6	44.5
Soil + cow dung + 129 lbs N per acre + 1 % KCL	24.1	44.1

DISCUSSION

The above results clearly show that the addition of potassium chloride partially checks the loss of nitrogen from ammonium sulphate when applied to soil along with organic matter. The ammonium ions added to the soil undergoes nitrification as follows:—



During this process an unstable substance ammonium nitrite may be formed which decomposes and loses nitrogen according to the following reaction:—



Therefore there appears to be a considerable loss when ammonium sulphate is added to the soils but in presence of potassium ions, there is always the possibility of formation of more stable substance potassium nitrite instead of ammonium nitrite. That is why the loss of nitrogen from ammonium sulphate in presence of potassium chloride appears to be less (8).

ACKNOWLEDGEMENT

I am grateful to Prof. N. R. Dhar for his keen interest evinced in guiding the above work.

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SPECTROGRAPHIC ORBIT OF HD 221253

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[Received on 10th March 1959]

ABSTRACT

The spectrographic orbital elements for spectroscopic binary HD 221253 were computed from twenty six observations during the year 1957. From Petrie's previous determinations the period is taken as 6.066278 days. The other elements computed are :

$$T = \text{J. D. } 2436120.026 \pm 0.054, e = 0.22 \pm 0.02$$

$$\omega = 43.20 \pm 3.6^\circ \text{ K} = 52.5 \pm 0.9 \text{ Km/sec.}$$

$$\text{and } V_0 = -9.4 \pm 0.7 \text{ Km/sec.}$$

period of apsidal motion is obtained as 450 ± 100 years. The computed mass of 9.6 solar masses is obtained for the primary star which is of spectral type B4. The estimated mass of the secondary is 2.3 solar masses.

INTRODUCTION

The star HD 221253, the position of which in the sky is given by $\alpha_{1900} = 23^{\text{h}} 25^{\text{m}}$ and $\delta_{1900} = +58^\circ 00'$, was discovered to be a spectroscopic binary by Frost and Adams (1903). The spectrum of this binary has very diffuse and broad lines. Only few lines are measurable. The spectrum of the secondary component is not observed at all. The primary whose spectrum is observed is a B4 star. The absolute magnitude of -1.3 is derived by Petrie from the measurements of equivalent width of H_γ for this primary.

The star seems to be peculiar in the sense that its orbital elements appear to be changing irregularly. The full details of these variations are under investigation by Petrie of Dominion Astrophysical Observatory Victoria. In the present note the orbital elements have been computed from the observations of 1957 only.

OBSERVATIONS

These spectrograms were obtained by Petrie during 1957 at the Dominion Astrophysical Observatory Victoria with two prism medium camera with focal length of 71 mm (II M). The dispersion acquired in these spectrograms is as follows :

λ		dispersion in $\text{\AA}^\circ/\text{mm}$
Ca II (K)	...	9.2
4202	...	12.8
H_γ	...	14.8
4481	...	17.1

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The plates were measured for radial velocity by Andrews, a very careful and expert measurer with the help of a specially designed machine for this purpose. The Twenty six spectrograms used in the present computations are listed in the following Table I. Since all the plates almost look equally well equal weights were adopted for all the observations. The period of 6.066278 days has been taken from the previous determinations of Petrie. This period fits very well for the present observations also.

TABLE I
Observations of HD 221253

No.	J. D.	Observations		Standard 5 × 8 Scale	
		Phase from epoch	Radial velocity	Phase	Radial velocity
1	2436041.961	3.642	— 28.4	4.803	— 1.30
2	51.965	1.513	+ 24.4	1.995	+ 1.12
3	64.943	2.359	+ 49.3	3.111	+ 2.26
4	74.950	0.233	— 25.6	0.307	— 1.17
5	76.945	2.228	+ 48.5	2.938	+ 2.23
6	80.932	0.149	— 34.6	0.196	— 1.59
7	94.949	2.033	+ 44.6	2.681	+ 2.05
8	96.854	3.938	— 39.6	5.193	— 1.82
9	2436103.951	4.969	— 47.2	6.553	— 2.17
10	04.941	5.959	— 29.3	7.858	— 1.34
11	15.928	4.813	— 55.6	6.347	— 2.55
12	29.890	0.567	— 22.5	0.748	— 1.03
13	29.886	0.573	— 27.0	0.756	— 1.24
14	30.667	1.354	+ 14.4	1.786	+ 0.66
15	30.674	1.361	+ 23.4	1.795	+ 1.07
16	31.921	2.608	+ 39.8	3.439	+ 1.83
17	38.676	3.296	+ 0.4	4.347	+ 0.02
18	38.777	3.397	+ 1.6	4.480	+ 0.07
19	43.746	2.300	+ 61.3	3.033	+ 2.81
20	43.750	2.304	+ 64.2	3.038	+ 2.95
21	45.819	4.373	— 52.3	5.767	— 2.40
22	45.827	4.381	— 48.9	5.778	— 2.24
23	51.671	4.159	— 35.9	5.485	— 1.65
24	51.678	4.166	— 50.7	5.494	— 2.31
25	62.701	3.056	+ 19.3	4.030	+ 0.89
26	62.708	3.063	+ 24.8	4.039	+ 1.14

The adopted epoch of J. D. 2436117.1808 is the arithmetic mean of all dates of observations. The observed phases and velocities were changed to the standard scale used at the Dominion Astrophysical Observatory Victoria for comparison of these observed velocity curves with the standard theoretical curves. This comparison at once gives most of the preliminary elements. In particular one gets 'T' the time of periastron passage. Then one rearranges the observations according to the phases from T. In table 2 these observations are rearranged according to the phases from the final epoch T which is J. D. 2436120.026.

TABLE 2
Representation of Observations

No.	Phases from final T (days)	Observed radial velocity (Km/Sec)	$V_{\text{obs}} - V_{\text{cal}}(\text{Km/Sec})$
1	0.211	+ 19.3	- 3.7
2	0.218	+ 24.8	+ 2.4
3	0.451	+ 0.4	- 3.6
4	0.552	+ 1.6	+ 5.4
5	0.797	- 28.4	- 7.5
6	1.093	- 39.6	- 3.0
7	1.314	- 35.9	+ 8.7
8	1.321	- 50.7	- 5.9
9	1.528	- 52.3	- 2.7
10	1.536	- 48.9	+ 0.9
11	1.968	- 55.6	- 2.1
12	2.124	- 47.2	+ 6.0
13	3.114	- 29.3	+ 8.1
14	3.370	- 34.6	- 4.4
15	3.454	- 25.6	+ 2.1
16	3.788	- 22.5	- 6.2
17	3.794	- 27.0	- 10.9
18	4.575	+ 14.4	- 2.4
19	4.582	+ 23.4	+ 6.2
20	4.734	+ 24.4	+ 8.2
21	5.254	+ 44.6	- 1.0
22	5.449	+ 48.5	- 1.8
23	5.521	+ 61.3	+ 10.1
24	5.525	+ 54.2	+ 13.0
25	5.580	+ 49.3	- 2.2
26	5.829	+ 39.8	- 8.4

SOLUTION

Following preliminary orbital elements were obtained from the comparison of the observed velocity curve with the standard theoretical curves

$$T = \text{J. D. } 2436120.062$$

$$e = 0.25$$

$$\omega = 45^\circ$$

$$V_0 = -10.3 \text{ Km/Sec.}$$

$$K = 54.5 \text{ Km/Sec.}$$

These preliminary elements were corrected by least square solution using Lehmann Filhe's equation of condition. The period was considered to be sufficiently accurately known. These twenty six observations were grouped into following normal places.

TABLE 3
Representation of Normal Places

No.	Mean Phases (days)		Mean Observed Velocity (Km/Secs.)	Weights	$V_{\text{obs}} - V_{\text{cal}}$ (Km/Sec.)	
	Preliminary	Final			Preliminary	Final
1	0.1783	0.2146	+ 22.05	2	- 2.52	- 0.64
2	0.4654	0.5017	+ 1.00	2	+ 1.64	+ 0.94
3	1.0315	1.0678	- 34.63	3	+ 3.67	+ 0.91
4	1.4252	1.4615	- 50.63	3	- 0.07	- 2.29
5	2.0098	2.0461	- 51.40	2	+ 2.95	+ 2.00
6	3.2056	3.2419	- 31.95	3	+ 2.19	+ 2.00
7	3.6422	3.6785	- 25.03	2	- 4.32	- 4.83
8	4.5939	4.6302	+ 20.73	3	+ 2.43	+ 1.34
9	5.4901	5.5264	+ 51.28	6	- 2.24	+ 0.05

For these normal places, given in table 3, the Observation equations are as follows :

No.						
1	1.0000 x	+ 0.6294 y	+ 0.0470 z	+ 1.0685 u	+ 1.3660 v	+ 2.5200 = 0
2	1.0000	+ 0.1668	- 0.9496	+ 1.1768	+ 1.3806	- 1.6400
3	1.0000	- 0.5242	- 0.8157	+ 0.8899	+ 0.7161	- 3.6700
4	1.0000	- 0.7490	- 0.0007	+ 0.5550	+ 0.3085	+ 0.0700
5	1.0000	- 0.8187	+ 0.8237	+ 0.0818	- 0.0619	- 2.9500
6	1.0000	- 0.4478	+ 0.5456	- 0.6042	- 0.4411	- 2.1900
7	1.0000	- 0.2014	+ 0.0304	- 0.7490	- 0.5482	+ 4.3200
8	1.0000	+ 0.5145	- 1.0122	- 0.7645	- 0.7512	- 2.4300
9	1.0000	+ 1.1607	+ 0.3716	- 0.0018	- 0.2331	+ 2.2400

Where

$$x = \delta V_0$$

$$y = \delta K$$

$$z = -K \delta e$$

$$u = -K \delta \omega$$

$$v = \frac{+K \mu}{(1-e^2)^{3/2}} \delta T$$

$$\mu = \frac{360^\circ}{P}$$

These observation equations were reduced to the following normal equations.

$$\begin{array}{rcccccc} + 26.0000x & + 2.8969y & - 1.7164z & + 3.3740u & + 2.3713v & - 6.7200 = 0 \\ & + 14.2559 & - 0.0415 & - 1.1220 & - 1.5073 & + 26.1206 = 0 \\ & & + 9.9579 & - 2.8957 & - 3.3425 & + 16.5239 = 0 \\ & & & + 12.3370 & + 11.9300 & - 5.5913 = 0 \\ & & & & + 12.5792 & - 4.5932 = 0 \end{array}$$

The solution of these equations gave the following corrections to the preliminary elements.

$$\delta V_0 = + 0.31 \text{ Km/sec.}$$

$$\delta K = - 1.99 \text{ Km/sec.}$$

$$\delta e = - 0.033$$

$$\delta \omega = - 2^\circ.05$$

$$\delta T = - 0.0363 \text{ days}$$

This solution reduced the sum of the squares by 45%. Thus the following final values of the orbital elements were obtained together with their probable errors.

$$P = 6.066278 \text{ days (adopted)}$$

$$T = \text{J. D. } 2436120.026 \pm 0.054 \text{ days}$$

$$e = 0.22 \pm 0.02$$

$$\omega = + 43^\circ.0 \pm 3^\circ.6$$

$$V_0 = -9.4 \text{ Km/sec. } \pm 0.7 \text{ Km/sec.}$$

$$K = 52.5 \text{ Km/sec. } \pm 0.9 \text{ Km/sec.}$$

$$a \sin i = 4.272 \times 10^6 \text{ Km } \pm 0.077 \times 10^6 \text{ Km}$$

$$\frac{M_2^3 \sin^3 i}{(M_1 + M_2)^3} = 0.0846 \odot \pm 0.0046 \odot$$

These probable errors of the various elements were calculated in usual way. To facilitate the final comparison to see how each individual observation fits the

value of the velocity computed with the finally adopted orbital elements, the following curves has been constructed.

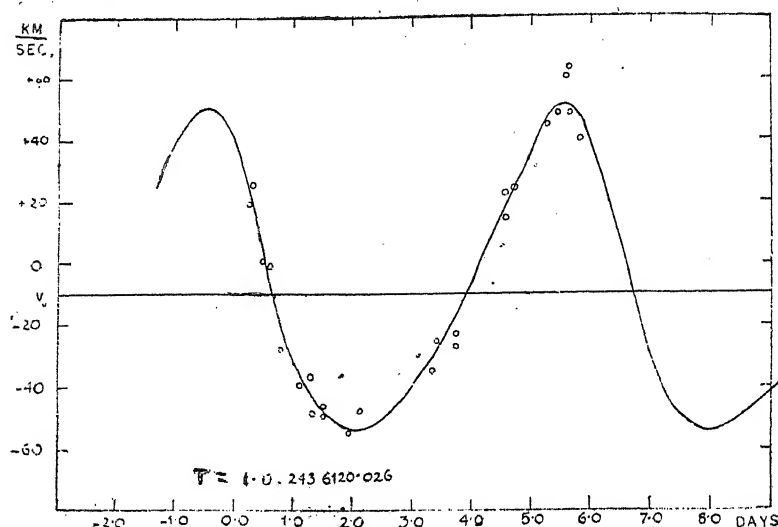


Fig. 1. The radial velocity curve of H. D. 221253 showing individual observations.

Baker (1908) has also derived the following elements

Period = 6.067 days \pm 0.0005 days

$e = 0.224 \pm 0.025$

$T = \text{J. D. } 2418223.762 \pm 0.128 \text{ days}$

$\omega = 3^\circ 35' \pm 8^\circ 17'$

$V_0 = -14.78 \text{ Km/sec.}$

$K = 59.06 \text{ Km/sec.}$

$a \sin i = 4,920,000 \text{ Km}$

From these the period of rotation of the line of apses has been computed. This comes out to be 450 years \pm 100 years.

The bolometric absolute magnitude of H. D. 221253 is -3.94 (1953). Applying the correction for temperature term one gets M_e from the following equation:

$$M_e = M_B + 2 \log \frac{T_e}{5200}$$

Using Kuiper's (1938) temperature scale one gets $M_e = -2.9$ for this star. From this the mass can readily be computed from Petrie's (1950) mass luminosity relationship given as follows:

$$\log \text{Mass} = 0.548 - 0.144 M_e + 0.002 M_e^2$$

Thus the computed mass of 9.6 solar masses is obtained for the primary star which is of B4 type of spectral class.

To estimate the mass of the secondary star whose spectrum is never observed the orbital inclination of $84^{\circ}9$ (1950) is adopted for this system. Thus the observed mass function gives M_2 as 2.3 times the solar mass. Again from the mass luminosity relation one gets $M_2 = +1.3$. Consequently it is quite clear that the secondary star is a dwarf star of A type which is about four magnitudes fainter than the primary. This explains also why one would never be able to observe the spectrum of the secondary star.

To summarise one can say from this analysis that the system of H. D. 221253 in all its probability consists of a B type primary star of mass 9.6 times the solar mass accompanied by a A type companion of mass approximately 2.3 times the solar mass. The two stars differ in luminosity by about four magnitudes so that the secondary spectrum could only be detected if at all by a very careful colour measurements in the red region.

ACKNOWLEDGEMENT

The author is very much indebted to Dr. Petrie from whom the measurements of the radial velocities were obtained. Author also expresses his thanks to Dr. Pearce for his very kind assistance in calculations and also other valuable discussions during the preparation of his paper. Thanks are also due to the Dominion Astrophysical Observatory for providing the other facilities for working there.

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REPEATED WASHING OF SOILS WITH NEUTRAL SALT SOLUTIONS

By

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[Received on 11th May, 1959]

ABSTRACT

Three soils were washed repeatedly with 0.01M neutral salt solutions of NaCl, KCl, Na₂SO₄ and K₂SO₄ at 1:2 soil-solution ratio and the outgo of calcium ions from the soils was observed. As a result of successive washings, the soils were found to have a tendency to become alkaline, the degree of alkalinity depending on the organic matter and phosphate contents of the soils.

The soils have a tendency to become acidic as a result of continuous washing with distilled water.¹ However, very dilute salt solutions may bring about alkalinity, as is generally observed by cultivators while irrigating their fields with saline cana waters. The present investigations were undertaken to find out the effect of washing the soils repeatedly with neutral salt solutions of a rather high concentration in the laboratory to imitate irrigational practices with high salt contents.

EXPERIMENTAL

Three soils, designated as normal, garden and good soil were selected for the experiment. They were finely powdered, passed through a 100-mesh sieve and oven-dried. The chemical analyses of the soils were also made (vide table-1). The normal soil is poor in carbon, the garden soil is fairly supplied whilst the good soil is richest in carbon.

50 gms. of the powdered soil samples were weighed in glass stoppered bottles and shaken in a shaker with 100 ml. of dilute solutions of NaCl, KCl, Na₂SO₄ and K₂SO₄ of 0.01 M concentration. After shaking for two hours, the bottles were set aside. After 24 hours, filtration was completed over a Buchner funnel fitted with filter paper, using suction. The filtrate was analysed for calcium content. The pH of the filtrate was also determined. The soil on the filter paper was carefully transferred into the bottle, the volume was made upto 100 ml. with salt solution and shaking done as before. In this way the soils were washed many times. Finally the soils were washed with distilled water, oven-dried and analysed for their chemical constituents as well as for exchangeable bases. The pH of the washed soils were also determined using 1:2.5 soil-water ratio by a Beckman pH-meter.

Chemical analysis of the soils was made according to the standard methods outlined by Wright² and Piper³. The exchangeable bases were found using neutral normal ammonium acetate.⁴

TABLE 1(a)
Chemical analysis of the soils used

Chemical constituents %	Soils		
	Normal	Garden	Good
HCl-insoluble	81.64	79.94	74.220
Sesquioxides	11.17	9.860	9.830
CaO	0.992	2.800	4.080
MgO	1.158	1.730	1.774
K ₂ O	0.735	0.987	0.995
P ₂ O ₅	0.079	0.1208	0.418
Total Carbon	0.400	0.670	1.659
Total nitrogen	0.041	0.076	0.249
Total carbonates as Ca CO ₃	1.24	3.950	4.64

TABLE 1(b)
Exchangeable bases and pH of the soils used

pH			Exchangeable bases m. e./100 gms.			
			Ca	Mg	K	Na
Normal soil	...	7.6	22.76	3.62	2.43	0.40
Garden soil	...	8.0	44.64	3.62	2.00	1.00
Good soil	...	7.6	48.71	6.94	3.14	0.84

TABLE 2
Washing the soils with 0.01M NaCl solution

No. of washings	Calcium given out per 100 gms. of soils washed					
	Normal soil	pH	Garden soil	pH	Good soil	pH
1	0.0330	7.5	0.0322	7.8	0.0480	7.3
2	0.0300		0.0240		0.0327	
3	0.0280		0.0180		0.0200	
4	0.0300		0.0180		0.0192	
5	0.0280		0.0100		0.0128	
6	0.0250		0.0120		0.0128	
7	0.0250		0.0130		0.0120	
8	0.0200		0.0156		0.0124	
9	0.0200	7.2	0.0180		0.0126	
10	0.0246		0.0180		0.0128	
11	0.0200		0.0180		0.0124	
12	0.0180		0.0150		0.0128	
13	0.0120		0.0150		0.0112	
14	0.0140	7.0	0.0180	8.0	0.0096	7.3
15	0.0106		0.0183		0.0084	
16	0.0086		0.0183		0.0108	
17	0.0093		0.0280		0.0080	
18	0.0100		0.0300		0.0092	
19	0.0120	7.0	0.0300	7.9	0.0108	7.3
20	0.0100		0.0298		0.0108	
21	0.0140		0.0258		0.0076	
22	0.0113		0.0200		0.0076	
23	0.0093		0.0200		0.0080	
24	0.0080		0.0200		0.0070	
25	0.0060		0.0180	7.9	0.0056	7.3
26	0.0060		0.0100		0.0078	
27	0.0053	7.0	...		0.0080	
28	0.0050		...		0.0092	
29	0.0040		...		0.0086	
30	0.0040		...		0.0080	
31	0.0043		...		0.0076	
32	0.0032		...		0.0104	7.3
33	0.0038	7.0	...		0.0080	
Mean :	0.0144		0.0200		0.0145	
pH of washed samples	8.5		8.5		8.2	

TABLE 3
Washing the soils with 0.01M KCl

No. of Washings	Calcium given out per 100 gms. of the soils					
	Normal soil		Garden soil		Good soil	
1	0.0228	7.4	0.0660	7.6	0.0337	7.4
2	0.0212		0.0359		0.0200	
3	0.0195		0.0260		0.0192	
4	0.0100		0.0200	7.8	0.0160	
5	0.0145		0.0200		0.0152	
6	0.0145		0.0200		0.0158	
7	0.0093	7.3	0.0196		0.0120	
8	0.0090		0.0216		0.0090	
9	0.0087		0.0216		0.0124	7.4
10	0.0100		0.0200		0.0106	
11	0.0065		0.0200	7.9	0.0108	
12	0.0059		0.0212		0.0108	
13	0.0059		0.0180		0.0112	
14	0.0052	7.3	0.0187		0.0108	
15	0.0052		0.0132		0.0104	
16	0.0060		0.0157		0.0124	
17	0.0062		0.0135	7.9	0.0076	
18	0.0042		0.0106		0.0070	7.4
19	0.0049		0.0140		0.0070	
20	0.0036		0.0130	7.9	0.0074	
Mean	0.0095		0.0210		0.0129	
pH of the washed soil samples	8.1		8.4		7.8	

TABLE 4

Washing the soils with 0.01M Na₂SO₄

No. of washings	Calcium given out per 100 gms. of the soils washed					
	Normal soil		Garden soil		Good soil	
1	0.0393	7.5	0.0398	7.9	0.0306	7.4
2	0.0320		0.0380		0.0256	
3	0.0320		0.0260		0.0240	
4	0.0320		0.0200	8.0	0.0210	
5	0.0300		0.0320		0.0189	7.6
6	0.0240	7.6	0.0220		0.0150	
7	0.0200		0.0200		0.0140	
8	0.0180		0.0240	8.0	0.0130	
9	0.0180		0.0230		0.0190	
10	0.0100	7.6	0.0180	8.0	0.0170	7.6
Mean	0.0255		0.0254		0.0213	
pH of washed samples	8.2		8.6		7.9	

TABLE 5

Washing of the soils with 0.01 M K₂SO₄

No. of washings	Calcium given out per 100 gms. of the soils		
	Normal soil	Garden soil	Good soil
1	0.0890	0.0680	0.0420
2	0.0514	0.0384	0.0320
3	0.0480	0.0340	0.0330
4	0.0440	0.0300	0.0320
5	0.0400	0.0290	0.0300
6	0.0320	0.0240	0.0240
7	0.0300	0.0180	0.0250
8	0.0240	0.0180	0.0176
9	0.0180	0.0100	0.0154
10	0.0180	0.0110	0.0080
Mean	0.0394	0.0279	0.0237
pH of washed samples	8.3	8.7	7.9

TABLE 6
Chemical analyses of the washed soils

Constituents %	Normal soils					Garden soil					Good soil				
	NaCl	KCl	Na ₂ SO ₄	K ₂ SO ₄	NaCl	KCl	Na ₂ SO ₄	K ₂ SO ₄	NaCl	KCl	NaCl	KCl	Na ₂ SO ₄	K ₂ SO ₄	
HCl-insoluble ...	83.52	81.98	82.00	82.01	81.00	81.00	80.3	80.4	79.30	77.85	76.1	77.0			
Sesquioxides ...	9.73	11.13	11.11	11.11	10.30	9.60	9.8	9.7	9.10	8.77	9.1	9.1			
CaO ...	0.329	0.733	0.635	0.441	2.10	2.22	2.44	2.40	3.380	3.58	3.79	3.75			
MgO ...	1.108	1.130	1.130	1.13	1.650	1.67	1.66	1.67	1.640	1.67	1.70	1.71			
K ₂ O ...	0.710	1.05	0.650	1.01	0.970	1.16	0.91	1.10	0.978	2.40	0.90	1.20			

TABLE 7
Exchangeable bases and pH of the washed soils

Exchangeable bases (m.e./100 gms)	Normal soils					Garden soil					Good soil				
	NaCl	KCl	Na ₂ SO ₄	K ₂ SO ₄	NaCl	KCl	Na ₂ SO ₄	K ₂ SO ₄	NaCl	KCl	NaCl	KCl	Na ₂ SO ₄	K ₂ SO ₄	
Ca ...	12.80	16.04	19.86	16.73	35.90	40.06	40.40	40.15	36.20	36.39	43.60	42.31			
Mg ...	2.00	3.20	3.40	3.40	2.40	2.45	3.40	3.10	4.87	3.43	6.00	59.0			
K ...	2.00	3.20	2.10	4.10	1.80	2.73	2.00	3.10	2.10	7.40	3.00	5.10			
Na ...	2.30	0.00	3.00		3.00		3.30	0.40	3.00	...	1.00	0.00			
pH ...	8.5	8.1	8.2	8.3	8.5	8.4	8.6	8.7	8.2	7.8	7.9	7.9			

DISCUSSION

The foregoing results clearly show that as a result of successive leaching with neutral salt solutions, the soils lose a great deal of calcium. This loss in calcium from the soils is mainly from two sources, firstly from the calcium carbonate present in the soils and secondly from the exchangeable calcium of the soils. The neutral salts of sodium and potassium are known to exert a dissolving action on calcium carbonate hence a good deal of calcium is lost from the calcium carbonate contained in the soils.

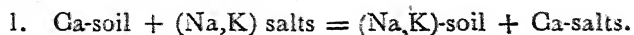
The neutral salts have a power to replace the cations contained in the exchange-complex of the soils, but very dilute solutions are comparatively less powerful. This is the reason that inspite of as many as 32 washings with 0.01M NaCl, the normal, garden and good soils lose only 10, 8.7 and 12.5 m.e. of exchangeable calcium per 100 grams of the soils respectively. The total losses of calcium from the soils are 0.662, 0.7 and 0.7% respectively (as calcium oxide). It is, therefore, obvious that 50% of the calcium losses from the soils are due to the calcium carbonate present in them and another 50% due to the exchange phenomena.

However, the losses from calcium carbonate are not directly proportional to their amounts present in the soils. The good soil which contains the maximum amount of CaCO_3 , loses an equivalent amount of calcium as the garden soil or the normal soil which contain lesser amounts of calcium carbonate. It is, therefore, evident that other factors influence the losses of calcium from the soils. The good soil is very rich in organic matter and phosphate contents whilst the normal soil is poorest in them. The garden soil stands in the midst, therefore, it appears that the losses of calcium are greatly minimised from the good soil due to its being well supplied with organic matter and phosphate inspite of its high calcium content. The normal soil which is deficient in total carbon and phosphate, loses the maximum amount of calcium, if we take into account the percentage of calcium lost from the total amount of calcium present in the soil.

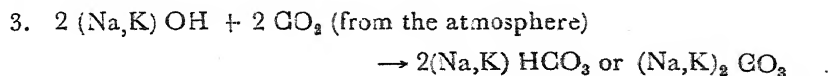
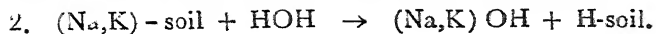
From table 7, it is also clear that the pH of the three soils has increased as a result of washing the soils repeatedly with dilute solutions of neutral salts of sodium and potassium. The increase in pH value of the normal soil is from 7.6 to 8.5, from 8.0 to 8.5 in the garden soil whilst in the case of good soil the increase is from 7.6 to 8.2, when 0.01M NaCl is used for washings. These increases are dependant upon the milliequivalents of sodium ions which have entered the exchange-complex as a result of base-exchange. From the table, it is also clear that practically equal amounts of sodium ions have entered into the exchange-complex of the three soils. However, the good soil is least alkaline, because the amount of sodium in the complex is relatively low when considered as a percentage of the total exchangeable bases. The production of alkalinity as a result of the entry of sodium-ions depends a great deal on their relative amounts in exchange-complex and also on the extent of their hydrolysis. Potassium salts behave in a similar manner as the sodium salts, hence an increase in the pH values of the washed samples is also observed. In a recent communication⁵, attention has been drawn towards the occurrence of K-soils in nature, side by side the Na-soils, both being equally alkaline.

The pH values of the filtrates do not reveal any increase in the pH of soils, because in the presence of salts, the hydrolysis of Na or K-soils cannot take place.

The production of alkalinity in soils, as a result of washing with neutral salt solutions can take place :—



On removing the calcium salts and the free (Na,K) salts :—



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